METODS FOR SYNTHESIS OF NANOTUBES AND STRUCTURE (review article)

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Carbon nanotubes are discussed in this review structure and synthesis methods. Carbon nanotubes synthesis by variety methods and each of the mechanisms have precise features that can be specify properties of carbon nanotubes. Arc discharge, laser ablation and chemical vapor deposition are most common methods and mechano thermal, electrolysis and flame are others ways for synthesis carbon nanotubes.

Keywords: Carbon nanotubes, synthesis methods of carbon nanotubes, cvd, arc discharge,mechano thermal.
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Introduction

Nanoscience is the study, understanding and control of phenomena and manipulation of material at the nanoscale, so nanoscience is the world of atoms, molecules, macromolecules, quantum dots, and macromolecular assemblies. Research in nanoscience is an interdisciplinary knowledge which means that it is a whole knowledge on fundamental properties ofnanosized objects but not limited to physics, chemistry, biology, medicine, engineering, and materials science. Nanotechnology describes many diverse technologies and tools, which do not always appear to have much in common! Therefore, it is better to talk about nanotechnologies, in the plural (2). Carbon nanotubes (CNTs), composed of graphene/graphite sheets, have been used since the 1990s and become one of the most important materials owing to its massive applications in energy, environmental and life sciences.

Carbon nanotube (CNT) is one form of carbon, with nanometersized diameter and micrometer-sized length (where the length to diameter ratio exceeds 1000). The atoms are arranged in hexagons, the same arrangement as in graphite. The struc- ture of CNT consists of enrolled cylindrical graphitic sheet (called graphene) rolled up into a seamless cylinder with diam- eter of the order of a nanometer. It is understood that CNT is the material lying in between fullerenes and graphite as a quitenew member of carbon allotropes (3).

In the [1] article authors studied the structure of carbon nanotubes. Carbon nanotubes are members of the fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a CNT is cylindrical, the ends of some CNTs are open; the others are closed with full fullerene caps. CNTs name is derived from their size, since the diameter ofa CNT is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several micrometer in length. Commercial applications for CNT have been rather slow to develop, how- ever, primarily because of the high production costs of the bestquality CNTs.

The current huge interest in CNTs is a direct consequence of the synthesis of buckminsterfullerene C_{60}, and other fullerenes, in 1985. The discovery that carbon could form stable, or-dered structures other than graphite and diamond stimulated researchers worldwide to search for other new forms of carbon. The search was given new impetus when it was shown in 1990 that C_{60} could be produced in a simple arc evaporation apparatus readily available in all laboratories. It was using such an evaporator that the Japanese scientist ‘‘Sumio Iijima’’ discovered fullerene-related CNTs in 1991 (4). The tubes contained at least two layers (multi-walled carbon nano- tubes MWCNTs), often many more, and ranged in outer diameter from about 3 nm to 30 nm. They were invariably closed at both ends.

A scanning of some MWCNT is shown in 1993; a new class of CNT was discovered, with just a single layer. These (single-walled carbon nanotubes SWCNTs) are generally nar-rower than the multi-walled tubes, with diameters typically in the range 1–2 nm, and tend to be curved rather than straight.

It was soon established that these new fibers had a range of exceptional properties, and this lead to increase of research into CNTs. It is important to note, however, that nanoscale tubes of carbon, produced catalytically, had been known for many years before Iijima’s discovery. The main reason why these early tubes did not excite wide interest is that they were structurally rather imperfect, so did not have particu-larly interesting properties. Recent research has focused on improving the quality of produced CNTs (5).

Structure of CNTs

Carbon nanotubes are sheets of graphite that have been rolled into a tube. A graphene sheet can be in rolled more than one way, producing different types of CNTs, (graphene is an individual graphite layer).

CNTs are considered as nearly one-dimensional structures (1D buckytube shape) according to their high length to diameter ratio.

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Most important structures are SWCNTs and MWCNTs. A SWCNT is considered as a cylinder with only one wrapped graphene sheet while MWCNTs are similar to a collection of concentric SWCNTs. The length and diameter of these structures differ a lot from those of SWCNTs and, of course, their properties are also very different. The bondings in CNTs is sp^2 and consist of honeycomb lattices and are seamless structure, with each atom joined to three neighbors, as in graphite. The tubes can therefore be considered as rolled up graphene sheets.

The type of CNT depends on how the graphene sheet is oriented on rolling. This can be specified by a vector (called chiral vector), which defines how the graphene sheet is rolled up. Fig. 1 showing how a hexagonal sheet of graphite is rolled to form a CNT in a vector structure classification.

The vector is determined by two integers (n,m). Two atoms in a planar graphene sheet are chosen and one is used as origin. The chiral vector C is pointed from the first atom toward the second one and is defined by the relation (6)

$C = na_1 + ma_2$

Where: n and m are integers. a_1 and a_2 are the unit cell vectors of the two-dimensional lattice formed by the graphene sheets. The direction of the CNT axis is perpendicular to this chiral vector.

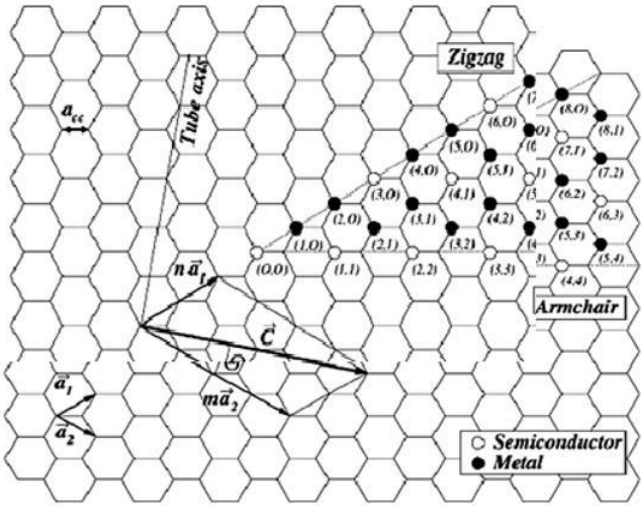

Fig. 1. The 2D graphene sheet diagram showing a vector structure classification used to define CNT structure.

Carbon nanotubes are only described by the pair of integers (n,m) which is related to the chiral vector. It can be seen from Figs. 1–3 three types of CNTs are revealed with these values:

$m = 0$ for all zig-zag tubes and (h = 30°);

$n = m$ for all armchair tubes and (h = 0°);

Otherwise, when $n \neq m$ they are called chiral tube and $(0° < h < 30°)$.

The value of (n,m) determines the chirality of CNT and affects the optical, mechanical and electronic properties. CNTs with $|n - m| = 3i$ are metallic like as in (10,10) tube, and those with $|n - m| = 3i \pm 1$ are semiconducting like as in (10,0) tube, (i is an integer)

The armchair and zig-zag tubes structures have a high degree of symmetry. These terms refer to the arrangement of hexagons around the circumference. While the chiral tube structure, which in practice is the most common, meaning that it can exist in two mirror-related forms.

The three distinct ways in which a graphene sheet can be rolled into a tube are shown in Fig. 2.

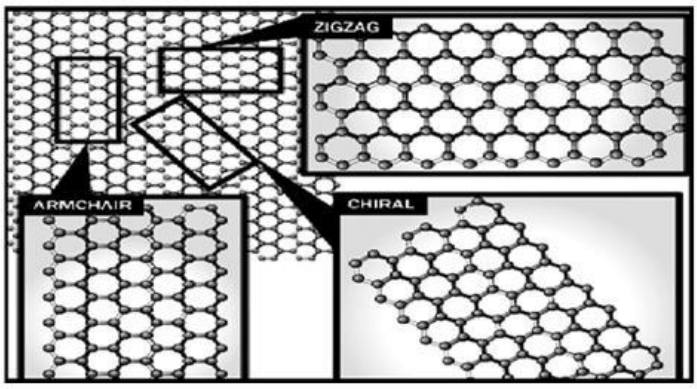

Fig. 2. Schematic diagram showing the way of formation different CNTs chirality structures.

For example; to produce a CNT with the indices, say, the sheet is rolled up so that the atom labelled (0,0) issuperimposed on the one labelled. CNTs structural types are shown in Fig. 3 .

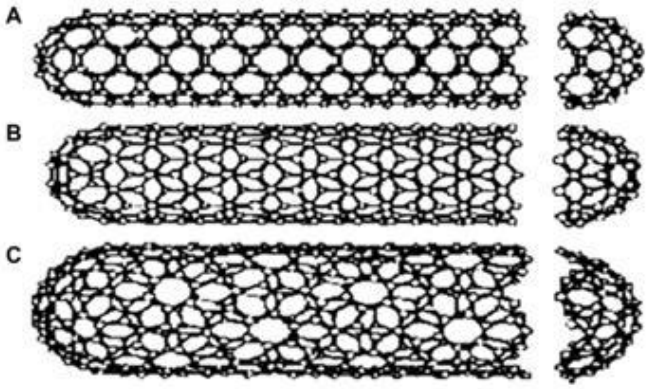

Fig. 3. CNTs structure with different chiralities. The difference in structure is easily shown at the open end of the tubes. (A) armchairstructure, (B) zig-zag structure, (C) chiral structure.

The terminating cap of CNT is formed from pentagons and hexagons. The smallest cap that fits on to the cylinder of the carbon tube seems to be the well-known C_{60} hemisphere. The smallest experimental value of CNT diameter of 0.7 nmis in good agreement with this cap (6). However, some authors have recently studied CNTs at the the- oretical limit of 0.4 nm in diameter. These CNTs are sometimes capped with a C_{20} dodeca-hedron.

Specific surface area gives good information of CNT characteristics and properties. Using some geometrical calcula- tions, the theoretical external specific surface area for CNTs have been determined. For one side of graphene sheet, the value obtained is 1315 m^2g^{-1} but using different multi-walled geometries and nanotubes bundles the va- lue decreases to 50 m^2g^{-1}.

The easiest way to visualise how CNTs are built up is to

start with graphite, the most stable form of crystalline carbon. Graphite consists of layers of carbon atoms. Within the layers, the atoms are arranged at the corners of hexagons which fill the whole plane (in the idealized case without defects). The carbon atoms are strongly (covalently) bound to each other (carbon–carbon distance 0.14 nm). The layers themselves are rather weakly bound to each other (weak long-range van der Walls-type interaction, interlayer distance of 0.34 nm). The weak interlayer coupling gives graphite the property of a seemingly very soft material, the property which allows using graphite in a pen to write with.

The nature of the bonding of a CNT is described by applied quantum chemistry, specifically, orbital hybridisation. The chemical bonding of CNTs is composed entirely of sp^2 bonds, similar to those of graphite. This bonding structure, which is stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. CNTs naturally align themselves into ropes held together by van der Waals forces. Under high pressure, CNTs can merge together, trading some sp^2 bonds for sp^3 bonds, giving great possibility for producing strong, unlimited length wires through high pressure CNT linking (7).

In their (8) paper authors investigated the synthesis of carbon nanotubes.

Chemical vapor deposition (CVD): CVD is a technique in which the vaporized reactants react chemically and forms a nanomaterial product that is deposited on the substrate Figure 4.

Sources for carbon: The precursor for carbon nanotubes are hydrocarbon gases such as acetylene, ethylene, methane, etc. .

Substrate used: Substrates are materials on which the CNTS are grown. The commonly used substrates in CVD method are zeolite, silica, silicon plate coatedwith iron particles, etc.

Catalyst used: To produce single-walled carbon nanotubes metal catalyst nanoparticles such as iron, cobalt, nickel, molybdenum, iron-molybdenum alloys,etc. are used.

Sources for CVD used: Based on the heating source, the CVD can be:

- *Thermal activated CVD which is heated by IR radiation, RF heater, etc.*
- *Photo assisted CVD which is heated by Arc lamps, CO_2 laser, Argon ion laser, Nd:YAG laser, etc.*
- *Plasma assisted CVD which is heated by microwave radiation, etc.*

Conditions maintained: The following conditions are maintained inside thefurnace.

- *Temperature: 500–900°C.*
- *Inert gas atmosphere: Argon gas.*

Procedure for synthesis of CNTs by thermal CVD method

CNTs are synthesized by thermal CVD method by using hydrocarbon gas as car- bon source. In this method, a quartz tube is placed inside a furnace

maintained at high temperature (500–900°C) heated by RF heater. A crucible containing the substrate coated with catalyst nanoparticles is placed inside quartz tube filled with inert gas such as argon gas.

The hydrocarbon gas (carbon source) is pumped into the quartz tube which undergoes pyrolysis reaction and forms vapor carbon atoms. These carbon atoms bind to the substrate and join to each other by Vanderwaal force of attraction and grow as multi-walled carbon nanotubes (MWCNTs) on the substrate [23]. To synthesize single-walled carbon nanotubes catalyst nanoparticles of Fe, Co, Ni are used. The obtained CNTs are further purified to get the pure form of CNTs.

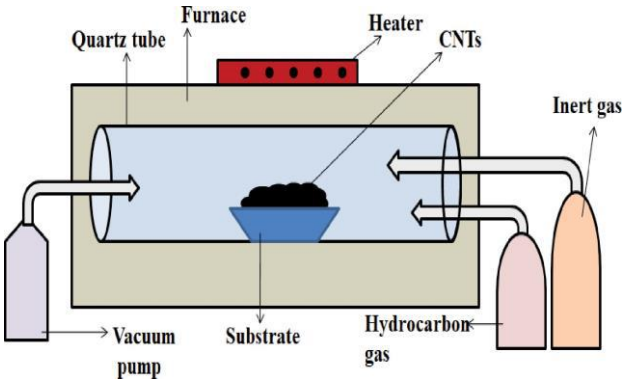

Fig.4. CVD method.

Electric arc discharge method

Carbon nanotubes are synthesized by electric arc discharge method which is also called Plasma Arcing method.

Electrodes: Pure graphite rods (both positive and negative electrode). The positive electrode is adjustable from outside to maintain the gap between the two electrodes.

Diameter of electrodes: 5–20 μm. **Gap between electrodes:** 1 mm. **Current:** 50–120 amperes.

Voltage: 20–25 V.

Inert gas pressure: 100–500 torr (No CNT formed below 100 torr). Inert gas is used for cooling and condensation of atoms to form the CNTs. Inert gas deter- mines the structure of carbons to be present in CNTS. Commonly used inert gas is helium gas.

Temperature: 3000–3500°C.

Reactor: It contains a quartz chamber which is connected to vacuum pump and a diffusion pump to inert gas supply. Initially the chamber is made vacuum by the vacuum pump and then the chamber is filled with helium gas by the diffusion pump [9].

Procedure for synthesis of CNTs by Electric arc discharge method

In this method, a potential of 20–25 V is applied across the pure graphite elec- trodes separated by 1 mm distance 4and maintained at 500 torr pressure of flowing helium gas filled inside the quartz chamber figure 5. When the electrodes are made to strike each other under these conditions it produces an electric arc. The energy produced in the arc is transferred to the anode which ionizes the carbon atoms of pure graphite anode and produces C^+ ions and forms plasma (Plasma is atoms or molecules in vapor state at high temperature). These positively charged carbon ions moves towards cathode, gets reduced and deposited and grow as CNTs on the cathode. As the CNTs grow, the length of the anode decreases, but the electrodes are adjusted and always maintain a gap of 1 mm between the two electrodes. If proper cooling of electrodes are achieved uniform deposition of CNTs are formed on the cathode which is achieved by inert gas maintained at proper pressure [10]. By this method multi-walled carbon nanotubes are synthesized and to synthesize single- walled carbon nanotubes catalyst nanoparticles of Fe, Co, and Ni are incorporated in the central portion of the positive electrode. The obtained CNTs are further purified to get the pure form of CNTs.

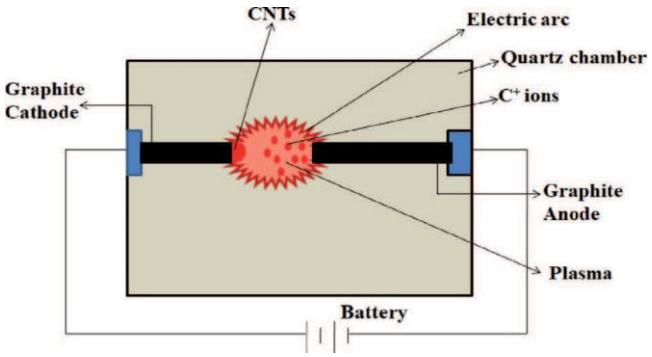

Fig. 5. Electric arc method.

Laser ablation method

Physical vapor deposition (PVD): PVD is a technique by which a material canbe vaporized into gaseous form and then deposited on the surface of a substrate.

Target source: The most common carbon source target used is solid graphitewhich is irradiated by laser source and vaporized into vapor carbon atoms.

Laser source: Laser source used for vaporization of target material into targetvapor atoms can be continuous laser source such as CO_2 laser or pulsed laser source such as Nd:YAG laser (Neodymium doped Yttrium Aluminum Garnet, Nd:$Y_3Al_5O_{12}$) .

Substrate used: The substrate used in this method is the water cooled copper collector on which the vaporized carbon atoms deposit and grow as CNTs.

Inert gas atmosphere: Argon gas is commonly used as inert gas which flows at a constant flow rate towards the water cooled copper collector.

Procedure for synthesis of CNTs by Laser Ablation method

Laser Ablation method is a Physical Vapor Deposition method in which graphite target is vaporized by laser source Figure 6. In this method the graphite target is placed at the center of quartz chamber filled with argon gas and maintained at 1200°C.The graphite target is vaporized by either continuous laser source or pulsed laser source. The vaporized target atoms (carbon) are sweeped toward cooled cop- per collector by the flow of argon gas. The carbon atoms are deposited and grown as CNTs on cooled copper collector. In case of continuous laser beam, the carbon atoms are continuously vaporized whereas in case of pulsed laser beam the amount of CNTs produced can be monitored as each shot of pulsed laser beam is directly proportional to the amount of carbon atoms vaporized [11]. By this method multi- walled carbon nanotubes are synthesized and to synthesize single-walled carbon nanotubes catalyst nanoparticles of Fe, Co, Ni are used.

The obtained CNTs are further purified to get the pure form of CNTs.

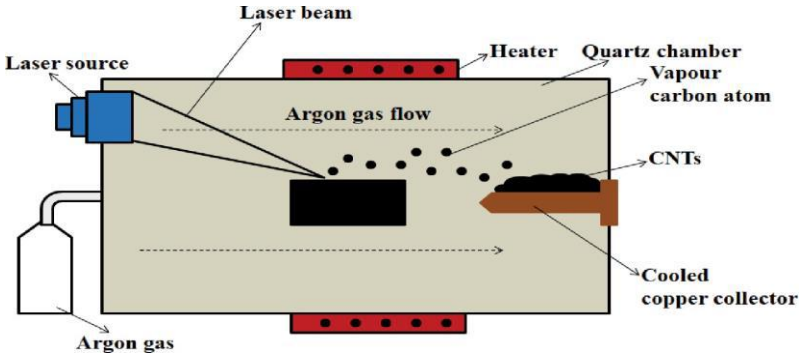

Fig. 6. Laser ablation method—schematic representation.

Procedure for pulsed laser deposition method

Pulsed Laser deposition is a thin film deposition technique in which the target material is vaporized by pulsed laser beam and vaporized target atoms are made to deposit on substrates Figure 7. The furnace contains a target at bottom and substrate mounted on the top. A pulsed laser beam from Nd:YAG laser source is made to strike the target to produce vaporized target atoms called the plume (plume is vaporized atoms at high temperature) [12]. The plume moves towards the substrate and it is deposited and grown as CNTs. Each shot of laser is directlyrelated to the amount of material ablated, thus deposition rate can be controlled and calibrated.

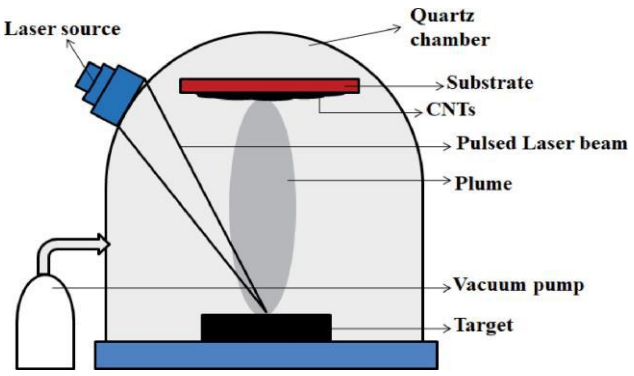

Fig. 7. Pulsed laser ablation method—Schematic representation.

The synthesis methods were investigated by Seyed Oveis Mirabootalebi, Gholam-Hosein Akbari Fakhrabadi. Authors (13).

First synthesis of cnt was done accidentally by arc discharge (1) and now synthesis methods of carbon nanotubes are different and various. Generally, produce type can specified properties of cnt (15); precursor (which can be solid, liquid, or gas), heat source, time, temperature, atmosphere of reactions and commonly; mechanism, determinate traits of cnt. Most common methods for synthesis of carbon nanotube are arc discharge, laser ablation and chemical vapor depositio n (15-19). Some of other methods for synthesis of carbon nanotubes include: dipping graphite in cold water (21), mechano-thermal (20), synthesis with decomposition Sic, torsion of graphene layers, with solar energy, synthesis with heat treatment of polymer, pyrolysis, with liquid phase and electrolysis.

Electrolysis method

This method based on liquid phase which was invention in 1995. with electrowinning of alkali or alkaline-earth metals from their chloride salts, cnt deposited on substrate (22).

By applying DC voltage between two electrodes in chamber of molten alkali-alkaline earth metals, could be produced multi walled carbon nanotubes. Relation (1) show formation lithium carbide (23).

$$2Li^{+}+2e^{+}+2C\,(\text{graphite}) = Li_2C_2 \qquad (1)$$

By forming lithium carbide (Li_2C_2), synthesize of cnt can be started in liquid phase. Generally; diameter of cnt in this method was 2-10 nm and length of them is 0/5 micrometer or more was reported and amorphous carbon, carbon nanofibers, nanographites and encapsulate cnt are byproducts of this method (24). Obtained Cnt usually are multi walled, but also in some researches, produced single walled cnt (26)

Different salts, applied for producing cnt such as NaCl, LiCl, KCl, and LiBr (25).Current density, electrolysis regimes, time, molten salt and temperature are the controller parameters of reaction. By optimizing condition of process, the reaction yields up to 20- 40% increase for producing multi walled carbon nanotubes].

Electrolysis can be done in low temperature, don't need to advanced equipment, possibility to controlling process of synthesize, have high quality, having low energy consumption and also don’t suitable for mass production.

CVD method

Cvd method known as simple way with gas precursor that containing carbon such as CO_2 or C_2H_2, C_2H_4 and other hydrocarbons and temperature of cvd changing amount 350-1000 ˚C. Different parameters influence on cnt growth; such as: time and temperature of reaction, diameter of catalyst, rate and type of reactant gas .

Classification methods of cvd, based on energy source and categorization in various types; for example when heat source is thermal resistance, flame or infrared lamps, this cvd called thermalcvd and also mechanism and catalyst of process effective in nominated of cvd.

Common methods for synthesis cnt are: plasma enhanced PE-CVD[2], aerosol CVD AA-CVD[3], with aerogel, with alcohol catalyst assisted AC-CVD[4], with laser LCVD[5], water assisted WA-CVD[6], hot filament HF-CVD[7], oxygen assisted, with plasma radio frequency RF-PE-CVD[88], with plasma microwave MPE-CVD[9] and catalytic CVD or CCVD[10][23,40,41]. Figure (2) show variety methods of cvd for synthesis carbon nanotubes.

Using plasma leading to increase velocity of reactions and Main properties of plasma enhanced is lower temperature than other methods, whilst minimum temperature of normal cvd 500˚C reported, synthesis temperature of carbon nanotubes and carbon nanofibers by plasma assisted even 120˚C reported and also this type with comparison other low temperature methods, have better vertically growth.

In cvd with aerosol, aerosol using as catalyst which catalyst particles distribution on substrate and help to synthesis cnt on substrate (28) Many researchers reported this method synthesizing high quality single and multiwall carbon nanotubes (28-30).

In aerogel type, sediments deposition on aerogel. Efficiency of Aerogel cvd is high (200% weight percentage for single-wall). The key point for high efficiency is high surface area of aerogel and so increase performance of alumina catalyst.

In alcohol cvd, alcohols use as carbon source which Fe and Co catalyst put on zeolite and evaporated alcohol (often methanol and ethanol), splashing over catalyst particles.

Temperature of process is rather low (about 550˚C) that lower than other common cvd methods. Diameter of carbon nanotubes about 1 nm and efficiency of process is 40% . Due to the high purity, low production costs and high efficiency, this method can be used for mass production of carbon nanotubes.

In L-cvd; focusing a laser beam on a small portion of the substrate, prevents damage of substrate. We have more control over synthesis parameters and on the other hand does not need to warm upall the substrate.

In water assisted cvd, the amount of water entering the process can be controlled and with precise control of amount of water can be achieved over 7 mm length of cnt.

In oxygen assisted-cvd, with a certain proportion adding oxygen to other gasses, single walled cnt with high efficiency could be synthesised. In fact; by adding oxygen to hydrogen, can be more control over the process and stop destruction sp_2 bonds that led to the steady alignment growth of single-walled nanotubes.

Added oxygen also leads to the loss of amorphous carbon and other carbon impurities and

remove the destructive precursor role during the growth and on the other hand, increasing the purity and efficiency; however, this method for some catalysts like separate iron nanoparticles due to carbothermal reaction, is not suitable .

Mechano Thermal method

Mechano thermal containing two main steps; first producing amorphous carbon and subsequently, annealing them in vacuum furnace. Carbon amorphisation done by high energy ball milling. Milling time for synthesis amorphous carbon up to 180 h that change for different condition: difference in type of atmosphere (Ar or air), cup speed (300 rpm or more), ball to powder ratio, numbers of balls and purity of powders. With increasing milling time, crystallite size decreasing and finally forming amorphous structure.

With attention to long time of milling, very small amount of metal powders due to Friction between the cup and balls, enter the graphite powder and possibility help to nucleation and growth of cnt in thermal step.

Produced amorphous carbon putting in vacuum furnace. Temperature of furnace 1400˚ C for a few hours to connecting atoms of amorphous carbons together and forming carbon nanotubes. Structure of produced carbon nanotubes is usually springy multi walled nanotubes.

Properties of Mechano-thermal includes: simple process, suitable for mass production, low cost, and don't need to special equipments, butt the time of process is too long and mechanism of process is not continuous and inclusive two steps.

Laser Ablation method

In Laser ablation/vaporization, by strike pulsed laser or continuous wave laser on graphite target; nucleation and growth of carbon nanotubes to be started (31,23). First formation a hot evaporation and subsequently quickly cooled.

During cooling of the samples, small molecules and carbon atoms quickly condense and form larger clusters and synthesized carbon nanotubes by van der waals forces stay together. For producing multi wall carbon nanotubes use pure graphite rods and for single wall use composite block of graphite. For producing single walled, Graphite composited with metal catalyst, such as Fe, Ni and Co and He-H_2 and Ar use as ambient gas.

In pulsed laser, needs more intensity laser's light than continuous laser. Nd:YAG and CO_2 are most common lasers used for laser ablation (31).

Diameters of cnt which produced by this method 4-30 nm and length of them is about 1 micrometer. Byproducts and impurities are amorphous carbon, catalyst particles, fullerene etc. Catalyzers also help to growth of carbon nanotubes. Most of catalyst were used in laser ablation are: Co, Cu, Nb, Ni, Pt, Co/Ni, Co/Pt, Co/Cu, Ni/Pt. quality of production related to target composition , power of laser beam and laser properties, catalyst type, type of ambient gas , temperature of reactions and distance between substrate and target (31). Produced carbon nanotubes by this method have high purity, high yield and most produced single wall cnt; but not suitable for mass production and also need expensive and especial equipments .

Flame Synthesis

In this method, cnt synthesizing by direct combustion of carbon source in presence of an oxidizing gas (23). Generally; flame synthesis contain of three steps. First producing carbon source by hydrolysis of hydrocarbon. Second; diffusion of carbon's atoms to metallic catalyst and third; nucleation carbon nanotubes on surface of catalyst and it's gradual growth.

Oxidation gas can be oxygen or nitrogen and carbon feedstock are acetylene, methane, ethanol and ethylene. Type of flame created, have essential role on quality of produced carbon nanotubes and determinate amount of amorphous carbon in final producing. For optimizing condition, must be control temperature, composition of fuel gas and catalyst of reactions. This way is economic, suitable for mass production and most synthesizing single walled cnt, but rate of growth is relatively low.

Arc discharge

Arc discharge known as one of oldest method for producing carbon nanotubes (14). Two high purity graphite rods used as anode and cathode and by applied direct current (in some cases pulsed current), a stable arc is created. Due to the power of created arc, carbon separated from anode and condensed on cathode to forming of soot (23).

Arc discharge done in various environment such as: liquid environment (liquid nitrogen, toluene, not ionized water), gas environment (Ar, Ar-H, He) or in plasma rotating arc discharge. Plasma rotating arc discharge is an economic method for large-scale synthesis of carbon nanotubes. Centrifugal force which created by rotation, accelerating the evaporation of anode and also cause uniform and stable dispersion of arc and so increases volume and temperature of discharge plasma.

Most carbon nanotubes that synthesised by arc method are multi walled but by penetration graphite rods and filling them with graphite's powder and metal catalyst; can be achieve to single wallcarbon nanotubes.

Pressure of Steam chamber and flow rate; are two key parameters for controlling the process. In arc discharge; speed of process is high and synthesis condition is controllable, but both of quality of productions and efficiency of process is low.

The synthesis methods were analyzed by Nur-Azzah Afah Binti Taib , Sarawak Md. Rezaur Rahman, Mohammed Mahbubul Matin, Jamal Uddin, Muhammad Khusairy Bin Bakri, Afrasyab Khan Authors (30).

Laser vaporization method

The CNTs were first synthesized using a laser in 1995, and the pulsed laser vaporization (PLV) technique is used to extract a large variety of carbon allotropes from graphite, one of which is CNTs. A laser beam (Yttrium Aluminum Garnet or CO2 laser) was used in this process, and it will be put within a reactor, where it will be focused on the graphite rods. Until beginning the process, argon buffer gas and a catalyst mixture of Co and Ni in a 50:50 ratio was passed through the rod at 1200°C. The metal was added to the process to help catalyze the creation of SWCNTs, but it also produced a slew of other byproducts. As a result of the high temperature of the argon buffer steam, the rod will vaporize. As the vaporization was cooled, it was deposited in the copper collector, and nanotubes were formed (33,34). The schematic diagrams for the laser ablation procedure are shown in Fig. 8.

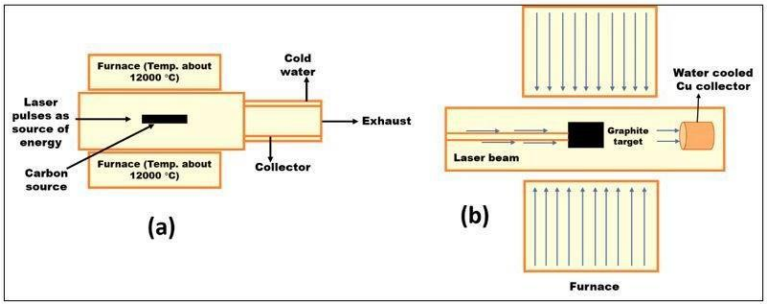

Fig. 8. Schematic diagram for laser ablation technique.

One of the benefits of this method is that high-quality SWCNTs with limited defects can be achieved in a reasonably high yield. Since the metallic atoms appear to vaporize when the tube's end is closed, this was possible. SWCNTs generated have excellent structural integrity as well. Furthermore, diameter modulation of the samples can be achieved easily by adjusting the method's parameters, i.e. catalytic metal, flow rate, and temperature. Apart from that, SWCNTs can be synthesized without requiring the production of MWCNTs .

However, there are several drawbacks to this approach. The CNTs generated may have some branching and may not be perfectly straight. Despite using higher purity graphite rods and laser forces, the amount of CNTs generated is lower than when the arc discharge approach is used (35). Typically, a significant amount of SWCNTs can be generated with good crystallization using both arc discharge and laser ablation methods. However, owing to the unique basic equipment requirements and high energy demand, these two strategies are less advantageous than CVD. In terms of yield and purity, CVD are superior to arc and laser methods. This is because the size of the carbon source, i.e., anode for arc discharge and target for laser ablation, determines the amount of the sample formed in both arc and laser processes. There is also a need for intensive purification of CNTs developed using these two techniques, which led to the production of gas phase methods like CVD .

Chemical vapor deposition (CVD) method

CVD is showing high potential to be used further as a CNTs processing tool for future industrial applications due to advantages such as relatively low growth temperature, high yields, and high purities with many explicit properties that can be obtained during its manufacture While this process was first used in the 1960s and 1970s to produce carbon fibers and carbon nanofibers, it was not until 1996 that it was used on a wide scale for the production and synthesis of CNTs. Strong, liquid, and gaseous precursors were used to aid in the development of CNTs at relatively low temperatures, i.e., 500 to 1000°C, and at atmospheric pressure. Metal or metal oxide catalyst particles are used as "seeds" to aid in the development of certain precursors. In addition, the gaseous or volatile carbon compound can decompose with the aid of metallic nanoparticles as a catalyst in this step. The catalyst also serves as a nucleation site for the development of CNTs . The reaction chamber is filled with a combination of nitrogen, ethylene, and acetylene during the procedure. This approach allows CNTs to expand in a variety of macroscopic morphologies, including powders and films (i.e., thick or thin), as well as various microscopic architectures (i.e., aligned, coiled, intertwined, or straight). The simplicity of the process is due to the use of such precursors, as well as different substrates and catalysts . As a result, producers will get the desired type of CNT. The four key parameters that specify the form of CNTs formed (SWCNT or MWCNT) in this process are the reactor's atmosphere, the source of hydrocarbon, the catalyst, and the growth temperature. MWCNTs are typically formed at lower temperatures (i.e. 600 to 900°C), while SWCNT development occurs at temperatures greater than 900°C. Not just that, but the commodity obtained is purer and has a higher yield. Regardless, defects can be detected in the composition of the samples collected, and these defects are normally in significant numbers. The general and basic schematic diagrams for the CVD technique are shown in Fig.9.

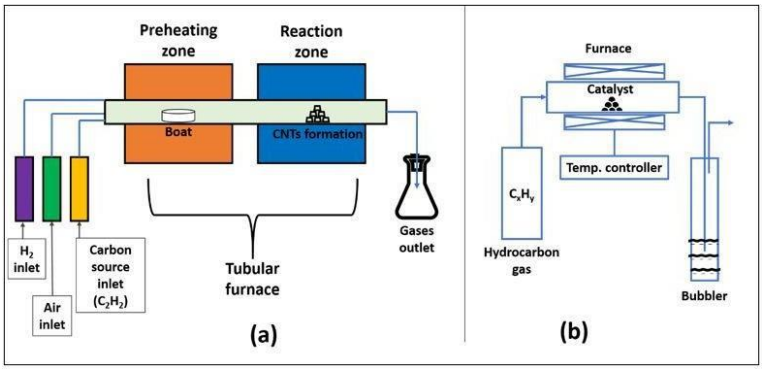

Fig. 9. Schematic diagrams of CVD process.

Thermal catalytic CVD

Decomposition of hydrocarbons or other carbon feedstock will take place at elevated temperatures ranging from 500 to 1200°C in this process. Prior to use, the feed would be dissolved in a steady flow of noble gases in the furnace, which would pass through transition metal catalysts such as iron, nickel, and cobalt, among others. The decomposed carbon would dissolve such metal particles until it reached a point of super saturation. The hydrocarbon is then decomposed and deposited on a substrate, i.e., alumina, glass, or silicon substrate. The carbon precipitate would then form in the shape of fullerene dorms. Depending on the temperature range of the process, different forms of CNT may be produced by using various types of carbon feedstock. Chemical composition and textural properties of the catalyst material(s) used are two parameters that control the length, diameter, orientation, and consistency of produced CNTs. The amounts of defects and the existence of amorphous carbon was also used to test the above properties of the finished product.

Plasma-enhanced CVD (PECVD)

PECVD is a broad concept that encompasses a variety of synthesis methods which may be either direct or remote. Direct PECVD was used to make MWCNT field emitter towers and some SWCNTs, while remote PECVD can be used to develop all types of CNTs. Instead of using thermal energy, this method uses energy sources that can supply energy for both hydrocarbon decomposition and CNT processing at a low temperature. The plasma energy sources used on the CNT formation are hot filament PECVD, direct current PECVD, radio frequency PECVD, and microwave PECVD. Hydrocarbon gas is used over intermediate metals in an ionized state in this process. Furthermore, the reactive species in the plasma system influenced the development of microscopic diameter tubes, which had implications for both diameter regulation and selective etching of metallic SWCNTs. The PECVD process consists of three major stages: (i) primary reaction takes place between energetic particles and carbon precursor in nonequilibrium plasma which leads to the precursor to be decomposed into carbon atoms and other active radicals; (ii) diffusion of carbon atoms and radicals onto the catalyst surface, as well as secondary reactions between the reactants, and (iii) catalyst interacts with the reactants on its surface, allowing carbon atoms to infiltrate and precipitate, as well as the release of result gases (Ding et al., 2016). This kind of CVD process has the benefit of producing a high yield of matched CNTs at a lower substrate temperature. Furthermore, by adding a voltage to the substrate, the volume of supplied ionized carbon species onto the catalyst surface can be tuned. The chirality distribution and growth rate of SWCNTs can be regulated, for example, by adjusting catalyst size and H_2 flow rate. This kind of CVD process has the benefit of producing a high yield of matched CNTs at a lower substrate temperature. Furthermore, by adding a voltage to the substrate, the volume of supplied ionized carbon species onto the catalyst surface can be tuned. The chirality distribution and growth rate of SWCNTs can be regulated, for example, by adjusting catalyst size and H_2 flow rate.

Alcohol CVD (ACCVD)

Since the temperature of the process is relatively low as low as 550°C, the ACCVD system can produce SWCNTs in large quantities at a low cost. Evaporated methanol and ethanol are applied to zeolite-supported iron and cobalt catalytic metal particles in this process. Alcohol reacting with catalytic metal particles created hydroxyl radicals, which removed carbon atoms with hanging bonds, preventing the formation of high-purity SWCNTs.

CONCLUSION

Nanomaterials provide an enriched knowledge on distinct probability and also definitely sound well in biomedical regenerative therapy for its uniqueness owing to its excellent physical as well as chemical properties.

Among of the main methods for synthesising carbon nanotubes, chemical vapour deposition due to simplicity, controllable mechanism, high ability for synthesizing aligned cnt, variety modified types for producing different kind of cnt, high efficiency close to 100% and suitable for mass producing; is the most attractive way for synthesis of carbon nanotubes.

Flame synthesis have high potential for producing economical large scale of cnt that have a simple mechanism; but increasing impurities is a big problem in this mechanism.

Laser ablation and Arc discharge are common method for synthesis cnt that both of them not suitable for mass production, besides that; quality of yields in arc discharge is low. The problem of mass production also exist for electrolysis, and this method used in laboratory scale. In mechano thermal despite simplicity and large scale of production, not continuous (consist of two steps) and process is very slow.

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